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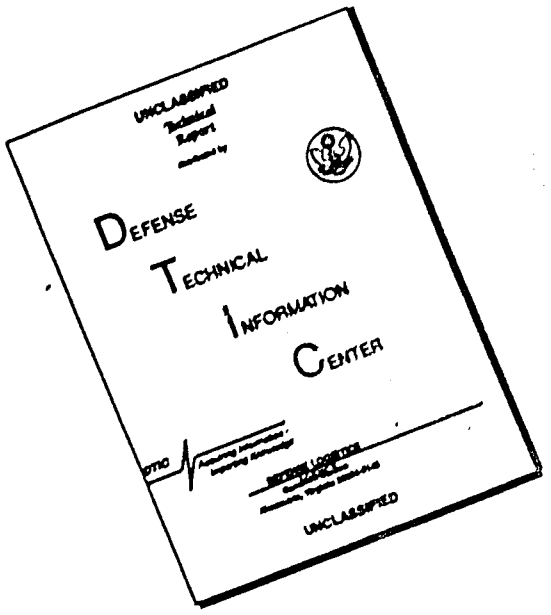

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POLAROGRAPHIC BEHAVIOR AND LARGE-SCALE ELECTROLYSIS OF SOME ALKYLNITROSAMINES

by

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ABSTRACT. The general behavior of dimethyl-, diethyl-, di-n-propyl-, and diisopropylnitrosamine was investigated at the dropping mercury electrode and the data obtained are discussed in a conventional polarographic manner. Diffusion-controlled waves were obtained in well-buffered media and in 20% ethyl alcohol solutions of either mineral or organic acids.

Yields of approximately 75% of 1,1-dimethylhydrazine were obtained by the large-scale electrolysis of dimethylnitrosamine at a mercury cathode in an organic acid solution of 4 to 5 pH. In 3N sulfuric acid solution, dimethylamine, ammonia, nitrous oxide, and nitrogen were established as reduction products, along with 50% yields of 1,1-dimethylhydrazine. Different mechanisms are proposed and discussed for the reduction of the alkylnitrosamines in acid, neutral, and alkaline solutions. Data indicate that the course of the reduction is complex and depends upon pH.

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FOREWORD

This report discusses the polarographic behavior, large-scale electrolysis, and the reduction mechanism of some alkylnitrosamines in acid, neutral, and alkaline solutions.

Since alkylhydrazines are of continuing interest in liquid propellant applications, it was believed desirable to make this study of the optimum conditions for preparing these compounds by the electro-chemical reduction of the alkylnitrosamines.

This work was supported in part by Foundational Research funds and was started in 1958.

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INTRODUCTION

Previous work by English and Heath and Jarvis has shown that dimethylnitrosamine can be determined polarographically (Ref. 1 and 2). Recently, data have been reported by Martin and Tashdjian on the polarographic reduction of some N-nitrosamines (Ref. 3). However, very little data were given by these investigators on the polarographic behavior of alkylnitrosamines in mineral or organic acids. They were unsuccessful in determining n-values directly and they did not isolate any products by large-scale electrolysis to help establish the true reduction mechanism. Probably the most thorough investigation of both the polarography and large-scale reduction of N-nitrosamines was made by Lund (Ref. 4) at about the same time work of this nature was being carried out in the laboratories of the U. S. Naval Ordnance Test Station. In general, where these research studies overlapped, good agreement of data was obtained.

In this report, additional information is presented on the polarographic behavior, large-scale electrolysis, and the reduction mechanism of some alkylnitrosamines. The course of the reduction is discussed in acid, neutral, and alkaline solutions and the optimum conditions for the preparation of the 1,1-disubstituted hydrazines are given.

EXPERIMENTAL

The N-nitrosamines used in this work were prepared by a nitrosation procedure similar to that described by Hatt (Ref. 5). The dimethylnitrosamine was purified by distillation at atmospheric pressure through an 18-inch Vigreaux column. The diethyl- and di-n-propylnitrosamine were purified by vacuum distillation through the same column. The diisopropyl- and diphenylnitrosamine were purified by recrystallization from 95% ethyl alcohol. The physical properties were as follows: dimethylnitrosamine, b.p. 146-147°C at 704 mm; diethylnitrosamine, b.p. 121-122°C at 140 mm; di-n-propylnitrosamine, b.p. 80-82°C at 2 mm; diisopropylnitrosamine, m.p. 45-46°C; and diphenylnitrosamine, m.p. 67-67.5°C.

Polarography

Polarograms were obtained with a Sargent Model XXI recording polarograph. Most solutions used in these studies had cell resistances of less than 600 ohms. Values of pH of the alcoholic and aqueous solutions were obtained with a Beckman Model G pH meter. Two capillaries were used in this work. The constants were 1.6 $mg^{2/3}sec^{-1/2}$ for capillary 1 and 1.4 $mg^{2/3}sec^{-1/2}$ for capillary 2 (Table 1). The capillary constants were determined in a McIlvaine's 2.4-pH buffer solution at -1.10 volts (vs. saturated calomel electrode, S.C.E.). Dissolved oxygen was removed from the solutions with nitrogen just prior to the polarographic examination. Small pyrex beakers (30 ml) were used as polarographic cells and all polarograms were obtained at 30°C. Half-wave potentials were referred to S.C.E. unless stated otherwise. When the mercury pool was used as a reference electrode, it was recognized that the data may not have exact significance; however, the data are reported for a relative comparison only. Diffusion currents were determined by the method of intersecting lines and Triton X-100 or gelatin were used as maximum suppressors.

Buffers of Britton and Robinson, Clark and Lubs, and McIlvaine were used during the investigations (Ref. 6 and 7). The McIlvaine's buffer was prepared five times normal strength. A stock solution of the N-nitrosamine was prepared in this buffer solution and diluted to a final concentration with the same buffer for polarographic study. Potassium chloride was added to the final polarographic solution where needed as an ionic strength agent. The salt of the respective acid was added to the final polarographic solution in the work with the mineral and organic acids (Table 2). When the buffers of Britton and Robinson or Clark and Lubs were used, the electrolysis solutions were prepared by adding aliquots of a stock N-nitrosamine solution to a 10-ml volumetric flask, adding 0.1 ml of 0.1% fresh gelatin solution and diluting to the mark with the aqueous buffer and ethyl alcohol. The solvents and reagents used in all studies were analytical grade.

TABLE 1. Half-Wave Potentials and Diffusion-Current Constants for 1.00 mM Solutions of Some Alkylnitrosamines[a]

Alkylnitrosamine	$E_{1/2}$ (vs. S.C.E.), v	$i_d/Cm^2/3t^1/6$
$(CH_3)_2N\text{-}NO$[b]	-0.953	8.6
$(C_2H_3)_2N\text{-}NO$[c]	-0.918	10.0
$n\text{-}(C_3H_7)_2N\text{-}NO$[c]	-0.871	8.6
$[(CH_3)_2CH]_2N\text{-}NO$[c]	-0.939	5.2

[a] McIlvaine's buffer of 2.4 pH.
[b] Capillary 1.
[c] Capillary 2.

TABLE 2. Half-Wave Potentials of Some Nitrosamines in Acid Media[a,b]

Compound	Conc., mM.	$E_{1/2}$ (vs. Hg pool), v		
		HCl	H_2SO_4	$HC_2H_3O_2$
$(CH_3)_2N\text{-}NO$	3.27	-1.00	-1.25	-1.46
$(C_2H_5)_2N\text{-}NO$	2.49	-0.92	-1.17	-1.42
$n\text{-}(C_3H_7)_2N\text{-}NO$	2.38	-0.97	-1.17	-1.39
$[(CH_3)_2CH]_2N\text{-}NO$	2.40	-0.94	-1.20	-1.47
$(C_6H_5)_2N\text{-}NO$	1.56	-0.66	-0.85	-1.08

[a] 20% ethanol, 0.35 N in acid, and 0.35 M in NaCl, Na_2SO_4 or $NaC_2H_3O_2$.
[b] Capillary 1.

Large-Scale Electrolysis

The large-scale electrolysis work was carried out in a divided cell of about 800-ml capacity. Three hundred ml of the supporting electrolyte were added to each compartment of the cell. About 25 ml of redistilled mercury were used as the cathode and a rotating-platinum electrode served as the anode. Five grams of the N-nitrosamine were added to the solution in the cathode compartment of the cell. Dry nitrogen was flushed through the catholyte for 10 minutes preceding the electrolysis and allowed to flow over the solution during the electrolysis. The potential applied to the cathode was controlled during the electrolysis with a potentiostat similar in design to that of Lingane and Jones (Ref. 8). Cathode potentials between -0.70 and -1.20 volts (vs. S.C.E.) were employed during this work (chosen as optimum from polarographic studies). Uniform stirring of the solution was maintained during the electrolysis by Cenco variable-speed stirrers. The pH of the catholyte was maintained fairly constant by periodic additions of either acid or base during the electrolysis. The reduction of the nitrosamine was followed polarographically or spectrophotometrically, and the run was stopped when the concentration of nitrosamine remaining in solution was negligible. The catholyte was removed from the electrolysis cell and diluted to volume in a 500-ml volumetric flask. Aliquots of this solution were analyzed for the 1,1-dialkylhydrazine by a direct titration procedure[1] with IO_3^- in the presence of $HgCl_2$; percent yields of the 1,1-dialkylhydrazines

[1] Unpublished work of H. W. Kruse, one of the co-authors of this report.

are based on this titration. Ten ml of concentrated sulfuric acid were added to the remaining catholyte and the solution was evaporated to near dryness (25–30 ml) in a 1-liter round-bottom flask. Sodium hydroxide was added to the flask so that the final solution was about 50% sodium hydroxide. The free bases were then distilled under vacuum and collected in cells for identification by infrared analysis. Gaseous products produced during the electrolysis were collected in evacuated gas sample bottles and submitted to a mass spectrometer analysis.

Recovery and identification of 1,1-dimethylhydrazine from the acid solution at the end of the electrolysis was made in the following manner: The catholyte from the reduction of dimethylnitrosamine in H_2SO_4 solution was evaporated with a rotary evaporator to about 100 ml in a round-bottom flask. Sodium hydroxide was added to the solution until the final mixture was approximately 50% in sodium hydroxide. Nitrogen was passed over the solution during the addition of the sodium hydroxide. The gases formed during the reaction were then passed into a solution of absolute ethanol saturated with dry HCl. The ethanol-HCL solution was filtered and the filtrate upon evaporation yielded a salt. The salt was placed in a separatory funnel, covered with about 50 ml of diethyl ether, and a saturated solution of sodium hydroxide was then added. The basic material liberated in this manner was retained by the ether. The sodium hydroxide solution was washed several times with ether and the ether extracts were combined and dried with anhydrous magnesium sulfate. The ether solution was then added to a saturated solution of oxalic acid in ether. A precipitate formed, which was then filtered, washed with ether, and twice recrystallized from absolute ethanol. This dried material had a melting range of 145.6-146.3°C and was identified as 1,1-dimethylhydrazine oxalate from a mixed melting point with an authentic sample.

RESULTS AND DISCUSSION

The half-wave potentials and diffusion-current constants of some alkylnitrosamines in acid solution are given in Table 1. The buffer capacity of the solution was sufficient to permit reduction of up to a 4.0-mM dimethylnitrosamine solution. One well-defined wave with no maximum was obtained in all cases. The $E_{1/2}$ values were obtained by plotting $E_{d.e}$ vs. log i/i_d-i. The $E_{d.e}$ values were corrected for iR drop through a cell whose resistance was 550 ohms. The dimethylnitrosamine appeared to be the most difficult to reduce of the alkynitrosamines investigated, while the n-propyl compound was the easiest. Diphenylnitrosamine was not investigated in this solution but was found to reduce easier than the alkylnitrosamines in both mineral and organic acid solutions (Table 2). Thus, the presence of a phenyl group lowers the half-wave potential as one would expect from the structure of the N-nitrosamines.

Effect of pH and Concentration on Half-Wave Potentials

The effect of pH on the half-wave potential of dimethylnitrosamine is shown in Table 3. The half-wave potential varies linearly with an increase in pH throughout the range from 0.8 to 3.6. The slope of the $E_{1/2}$ vs. pH plot in this pH interval was 0.136 volts per pH unit. It should be noted that poorly defined waves occur in the range from 3.6 to 6.0 pH and that the $E_{1/2}$ values become more negative and the slope of plots of pH vs. $E_{1/2}$ changes rapidly in the Clark's and Lubs' buffer system. With Britton's and Robinson's buffers, well-defined waves are found below a pH of 5.0; but in the range from 5.0 to 6.0 pH, poorly defined waves occur. Thus, poorly defined waves were found with each buffer system in the neutral or slightly acidic solutions. For quantitative analysis data the range below 2.0 pH is recommended. In general, the half-wave potentials of the alkylnitrosamines in acid solutions greatly depend upon pH while those in alkaline solution are independent of pH.

TABLE 3. Solution of 3.52 mM Dimethylnitrosamine in Clark and Lubs' Buffer System[a,b]

Apparent pH	$E_{1/2}$ (vs. Hg pool), v	i_d, μa	Wave definition
0.8	-0.94	44.4	Well
2.0	-1.05	44.4	Well
3.0	-1.20	33.8	Fairly well
3.6	-1.32	33.6	Poorly
4.0	-1.64	30.6	Poorly
5.0	....	....	Poorly
6.0	....	....	Poorly
8.0	-1.71	19.1	Well

[a] 20% ethyl alcohol, 80% buffer (2 X's).
[b] Capillary 1.

The half-wave potentials of dimethylnitrosamine solutions varied slightly with concentrations above 2-mM dimethylnitrosamine. However, in the range from 0.2 to 1.0 mM of dimethylnitrosamine the $E_{1/2}$ values were constant (Table 4). With diethylnitrosamine solutions from 1.0 to 2.0 mM the $E_{1/2}$ values varied in a linear manner.

TABLE 4. Effect of Concentration of the Half-Wave Potential and Diffusion Current Constant of Dimethylnitrosamine[a,b,c]

Conc., mM	i_d, μa	$E_{1/2}$ (vs. S.C.E.), v
0.2	2.56	-0.952
0.4	5.02	-0.952
0.6	7.92	-0.951
0.8	10.6	-0.952
1.0	13.4	-0.953

[a] No maximum suppressor or ethyl alcohol present.
[b] Capillary 2.
[c] McIlvaine's buffer of 2.4 pH.

Effect of pH and Concentration on Diffusion Current

The diffusion currents (i_d) appeared to be constant in strong acid solutions, where well-defined waves were observed. In weakly acidic and neutral solutions the waves were so poorly defined that accurate measurements could not be made. However, from Table 3 it would appear that i_d becomes less as the pH is increased from 2.0 to 8.0. The wave height at 8.0 pH is about one-half that found at 2.0 pH. At values above 8.0 pH, the diffusion current is fairly independent of pH. In general, the wave heights in alkaline solutions are about one-half those in acid solutions. These data would seem to indicate that the electrode reaction in alkaline solution requires fewer electrons and is a different process from that which occurs in acid solution.

It can be seen from Table 4 that in an aqueous solution at 2.4 pH the diffusion current of dimethylnitrosamine is substantially linear over the concentration range from 0.2 to 1.0 mM ($i_d = KC$). Solutions above 2-mM diethylnitrosamine appeared to vary slightly in a negative direction from linearity.

Effect of Mercury Height on Diffusion Current

In acid or alkaline buffered solutions, the limiting current of a solution of dimethylnitrosamine varies with the square root of the corrected mercury height, indicating a diffusion-controlled process. Two waves were observed for a 1.0-mM solution of dimethylnitrosamine in a 50% ethyl alcohol solution of tetramethylammonium chloride. The total diffusion current here was also found to vary as the square root of the height of the mercury ($i_d/h^{1/2}$ is constant). Thus, the polarographic waves obtained for the alkylnitrosamines in acid, alkaline, and neutral solutions appear to be diffusion-controlled.

Wave Form

The polarographic waves of the alkylnitrosamines are rather drawn out, as one usually finds with irreversible reductions. Diphenylnitrosamine solutions exhibited waves more nearly like those obtained with reversible processes. However, alkyl- and arylnitrosamine apparently reduce by irreversible processes. The wave form is very dependent upon pH, solvent, maximum suppressor, buffer components, and capillary drop time. Either one or two waves may be obtained. The waves in acid solution are larger and have a linear dependence upon pH, while in neutral and alkaline solution they appear to be smaller and independent of pH. It was observed that the wave form of a 50% ethyl alcohol solution of dimethylnitrosamine at constant ionic strength was particularly sensitive to very small changes in H^+ concentration (Table 5). From these data it would appear that the two waves observed are caused by the reduction in solution of two forms of the same molecule. Thus, the first wave is probably due to the reduction of a protonated specie while the second wave is probably due to the reduction of the free nitrosamine. It would also appear from the data (Table 5) that, in this acid solution at values < 2.50 pH, only the protonated specie exists. Diphenylnitrosamine solutions also exhibited the same behavior but the range in which only the protonated specie appeared to exist was < 3.20 pH. Two waves were obtained for the other alkylnitrosamines under identical conditions. In general, two waves were sometimes obtained in acidic and neutral solutions but only one wave was ever observed in alkaline solutions. Only the free nitrosamine specie undergoes reduction in alkaline solution. The $E_{1/2}$ value for the second wave (Table 5) also is very close to the $E_{1/2}$ value reported in Table 3 at 8.0 pH and would suggest that both these waves are due to the reduction of the free nitrosamine.

TABLE 5. Effect of H^+ Concentration on Waves of 3.30 mM N-Dimethylnitrosamine

The electrolyte was 0.5 M KCl-50% EtOH with 0.002% Triton X-100.

pH	$E_{1/2}$ (vs. Hg pool), v		i_d, μa		
	1st wave	2nd wave	1st wave	2nd wave	Total
3.30[a]	-1.14	-1.64	7.75	9.10	16.85
3.20	-1.15	-1.65	9.60	7.00	16.60
3.10	-1.15	-1.66	11.80	4.40	16.20
2.90	-1.16	-1.68	15.90	1.35	17.25
2.80	-1.17	....	.....	....	18.10
2.70	-1.19	....	.....	....	26.60
2.50	-1.19	....	.....	....	33.70
1.60[b]	-1.07	....	.....	....	33.80

[a] 5 drops of 0.1N HCl added to 10 ml of above solutions.
[b] 1 drop of concentrated HCl added to 2.50-pH solution.

Large-Scale Electrolysis

Large-scale reductions of the alkylnitrosamines were made in several different solutions. Table 6 presents data for dimethylnitrosamine. Various conditions of pH, temperature, and catholyte were used. It can be seen from these data that the optimum condition for preparing the 1,1-disubstituted hydrazine appears to be in an acetic acid-sodium acetate buffer solution of 5.0 pH at 25°C. About 75% yields of the 1,1-dimethylhydrazine were obtained in this manner. At values < 1.0 pH the yields of the alkylhydrazine were lower. For best yields of 1,1-dimethylhydrazine, the temperature of the catholyte should be maintained between 20–30°C and the pH of the solution should be controlled within the range from 1 to 5. In H_2SO_4-Na_2SO_4 solution (1.0 pH) approximately 50% yields of the 1,1-disubstituted hydrazines were obtained with di-n-propyl-, diisopropyl-, and diethylnitrosamine solutions. Thus, both mineral and organic acid solutions will give good yields of the 1,1-dialkylhydrazines. Table 6 also gives some data for reduction in alkaline solution. These data show that very little or none of the 1,1-disubstituted hydrazine is obtained in these solutions. Substantial amounts of the disubstituted amine and ammonia were found in these experiments.

TABLE 6. Electrochemical Reduction of N-Dimethylnitrosamine

Catholyte	pH	Temperature, °C	DMH,[a] % yield	Additional products found
Na_2SO_4-H_2SO_4	> 1.0	25–30	71.3	$(CH_3)_2NH$
H_2SO_4(3N)	< 1.0	25–30	53.0	$(CH_3)_2NH$, NH_3, N_2O, N_2
Na_2SO_4-H_2SO_4	> 1.0	45–50	60.2	$(CH_3)_2NH$, NH_3
Na_2SO_4-H_2SO_4	1-12[b]	25–35	35.3	$(CH_3)_2NH$
NaOAc-HoAc	4.8	20–30	78.0	$(CH_3)_2NH$, NH_3
NaOAc-HoAc	5.0	-2.0–+6.0	74.3	$(CH_3)_2NH$
NaOAc	11.5	25–30	4.0	$(CH_3)_2NH$, NH_3

[a] Yield of 1,1-dimethylhydrazine based on titration with IO_3^- in presence of $HgCl_2$.
[b] pH was not controlled during this run.

The solution from the reduction of dimethylnitrosamine in 3N H_2SO_4 (Table 6) was treated in the manner given in the experimental section. An infrared analysis of the gas showed that no formaldehyde, methylamine, methylhydrazine, or tetramethyltetrazene were present. However, ammonia, 1,1-dimethylhydrazine, and 1,1-dimethylamine were identified as present

in substantial amounts. Nitrogen and nitrous oxide were also identified as present from a mass spectrometer analysis. A chemical test made on a portion of the catholyte immediately after the electrolysis was completed, indicated no hydroxylamine was present (Ref. 9). Analysis of a 3N H_2SO_4 solution of dimethylnitrosamine indicated no loss of starting material occurred during the time of electrolysis by chemical decomposition of the nitrosamine in the strong acid.

Reduction Mechanism

When the diffusion coefficient of $D = 8.5 \times 10^{-6}$ cm^2 sec^{-1} (Ref. 3) was used and the validity of the Ilkovic equation was assumed, a value of n was calculated from polarographic data in acid solution (McIlvaine's buffer, 2.4 pH) for dimethylnitrosamine. This value of 4.72 was similar to that reported by Martin and Tashdjian (Ref. 3), who obtained values of n in this manner that varied from 3.7 to 5.3 in acid solution. These data would seem to indicate a 4 or 5 electron process was occurring. Therefore, a direct measurement of the n-value was made by a millicoulometric method (Ref. 10) in the 2.4-pH buffer solution. The average of five determinations by this method was found to be 4.96 with an estimated standard deviation of $\pm$ 0.10. The n-value of 5 suggested that the reduction mechanism in acid solution at the dropping mercury electrode may be a complex process. This assumption was indeed borne out by the results of the large-scale electrolysis experiments. Thus, it appears that the following electrode reactions may occur:

$$R_2NNO + 4e^- + 4H^+ \rightarrow R_2NNH_2 + H_2O \quad (1)$$

$$R_2NNO + 6e^- + 6H^+ \rightarrow R_2NH + NH_3 + H_2O \quad (2)$$

$$2R_2NNO + 6e^- + 6H^+ \rightarrow 2R_2NH + N_2 + 2H_2O \quad (3)$$

$$2R_2NNO + 4e^- + 4H^+ \rightarrow 2R_2NH + N_2O + H_2O \quad (4)$$

Since 1,1-dimethylhydrazine, dimethylamine, ammonia, nitrous oxide, and nitrogen were identified as products from the reduction of dimethylnitrosamine in 3N H_2SO_4, it seems likely that reactions 1–4 all occur in varying amounts at the mercury cathode during the electrolysis. However, the predominate reactions are apparently 1 and 2. As the pH is increased, reaction 1 is favored and as seen from Table 6 the best yields of 1,1-dimethylhydrazine are obtained in the range from 4 to 5 pH. As the pH is increased beyond 5 to the alkaline range, then reactions 2 and 4 are favored and very little of reaction 1 occurs. In strong alkaline solution it appears that reactions 1 and 3 are not favored.

In general, the course and degree of reduction of the alkylnitrosamines at a mercury cathode are dependent upon the pH of the electrolyte and are different in acid, neutral, and alkaline solutions.

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ABSTRACT CARD

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4 Chief of Naval Operations
1 Chief of Naval Research (Code 104)
1 Naval Air Engineering Center, Philadelphia
1 Naval Air Test Center, Patuxent River (Aeronautical Publications Library)
1 Naval Missile Center, Point Mugu (Technical Library)
1 Naval Ordnance Laboratory, Corona (Dr. Charles Maier)
  Naval Ordnance Laboratory, White Oak (Technical Library)
1 Naval Propellant Plant, Indian Head
  Dr. Bodo Bartocha (1)
1 Naval Research Laboratory
  Chemistry Division, Code 6100 (1)
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1 Naval Weapons Laboratory, Dahlgren (Technical Library)
  Office of Naval Research Branch Office, Chicago
  Office of Naval Research Branch Office, Pasadena
  Bureau of Naval Weapons Representative, Azusa, Calif.
1 Bureau of Naval Weapons Resident Representative, Sacramento
1 Chief of Ordnance (ORDTU)
  Aberdeen Proving Ground
    Ballistic Research Laboratories (1)
    ORDBG-BLI (1)
1 Army Missile Command, Redstone Arsenal (Redstone Scientific Information Center)
  Frankford Arsenal
    Propellants and Explosives Section, 1331 (1)
    Library (1)
1 Watervliet Arsenal (Library)
1 Radford Arsenal
1 Aeronautical Systems Division, Wright-Patterson Air Force Base (ASRMFP-Mat)
1 Advanced Research Projects Agency (Dr. G. V. Keck)
10 Armed Services Technical Information Agency (TIPCR)
1 Bureau of Mines, Pittsburgh (Reports Librarian)
1 Bureau of Mines, Region IV, Bartlesville, Okla. (Dr. John F. McCullough)
1 AeroChem Research Laboratories, Inc., Princeton, N. J.
1 Aerojet-General Corporation, Azusa, Calif. (Librarian), via BuWepsRep